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Synthesis and performance of Fe-based amorphous alloys for nuclear waste applications

L. Kaufman¹, J.H. Perepezko² and K Hildal²

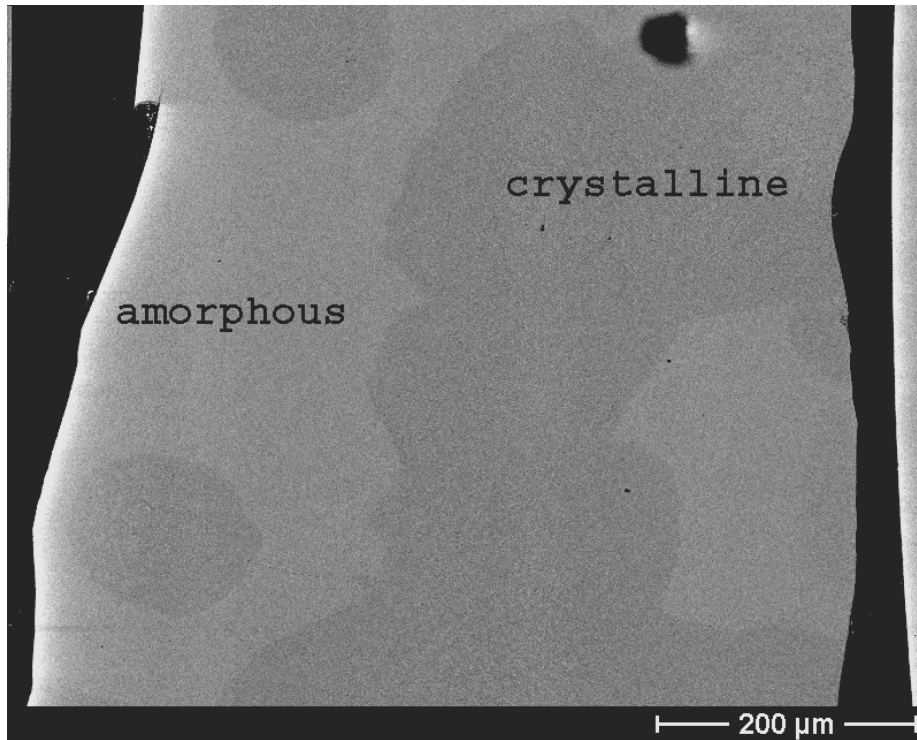
1- Larry Kaufman, Brookline, MA, 02445-5848

2- University of Wisconsin-Madison, Dept. Mat. Sci. and Eng., 1509 Univ. Ave.,

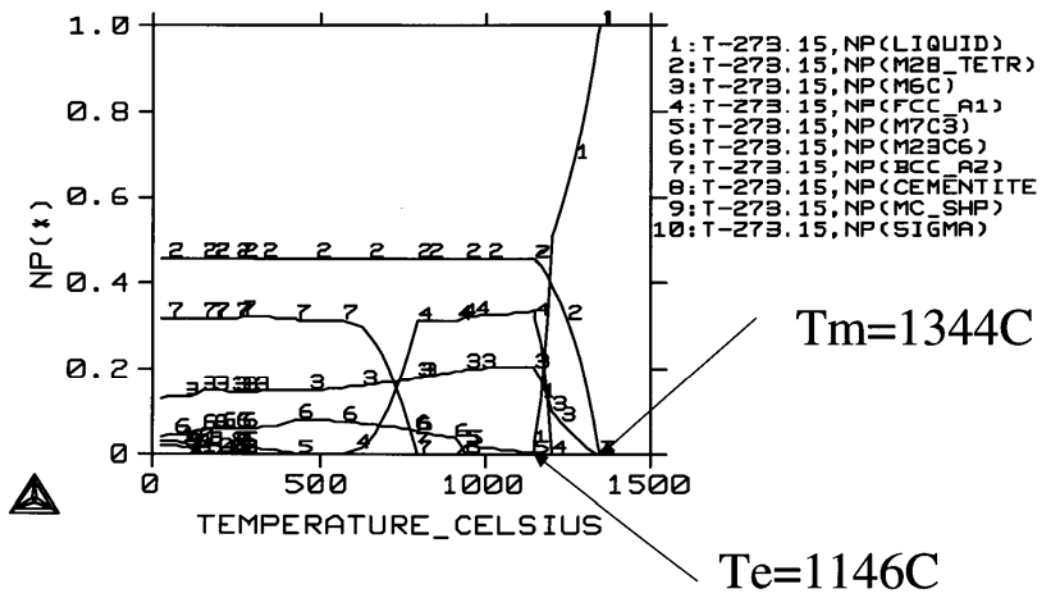
3- Madison, WI 53706

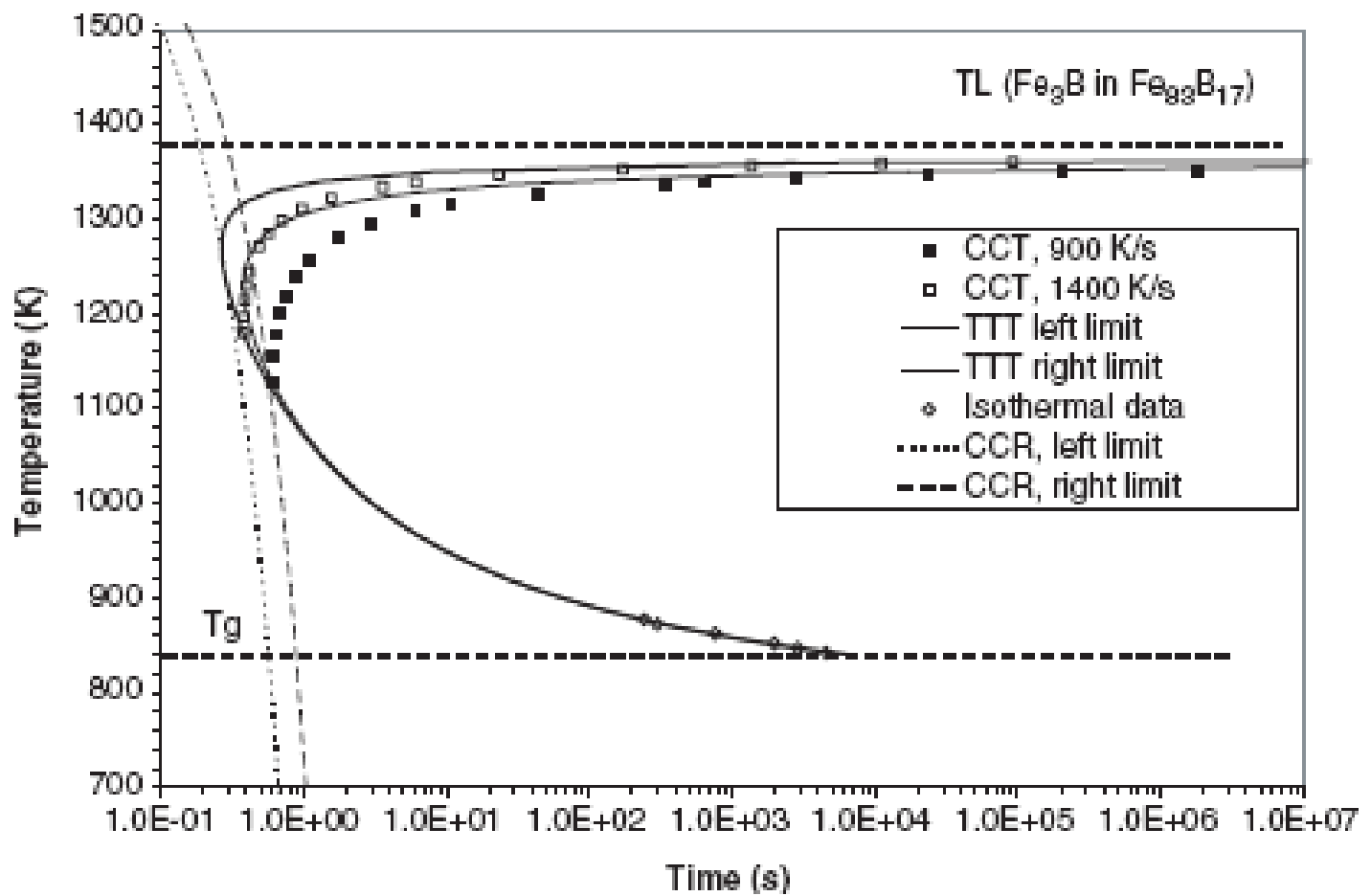
Recent developments in multicomponent Fe-based amorphous alloys have shown that these novel materials exhibit outstanding corrosion resistance compared to typical crystalline alloys such as high-performance stainless steels and Ni-based C-22 alloy. During the past decade, amorphous alloy synthesis has advanced to allow for the casting of bulk metallic glasses. In several Fe-based alloy systems it is possible to produce glasses with cooling rates as low as 100 K/s. At such low cooling rates, there is an opportunity to produce amorphous solids through industrial processes such as thermal spray-formed coatings. Moreover, since cooling rates in typical thermal spray processing exceed 1000 K/s, novel alloy compositions can be synthesized to maximize corrosion resistance (i.e. adding Cr and Mo) and to improve radiation compatibility (adding B) and still maintain glass forming ability. The applicability of Fe-based amorphous coatings in typical environments where corrosion resistance and thermal stability are critical issues has been examined in terms of amorphous phase stability and glass-forming ability through a coordinated computational analysis and experimental validation. For example, a wedge casting technique has been applied to examine bulk glass forming alloys by combining multiple thermal probes with a measurement based kinetics analysis and a computational thermodynamics evaluation to elucidate the phase selection competition and critical cooling rate conditions. Based upon direct measurements and kinetics modeling it is evident that a critical cooling rate range should be considered to account for nucleation behavior and that the relative heat flow characteristics as well as nucleation kinetics are important in judging ease of glass formation. Similarly, a novel computational thermodynamics approach has been developed to explore the compositional sensitivity of glass-forming ability and thermal stability. Also, the synthesis and characterization of alloys with increased cross-section for thermal neutron capture will be outlined to demonstrate that through careful design of alloy composition it is possible to tailor the material properties of the thermally spray-formed amorphous coating to accommodate the challenges anticipated in typical nuclear waste storage applications over tens of thousands of years in a variety of corrosive environments.

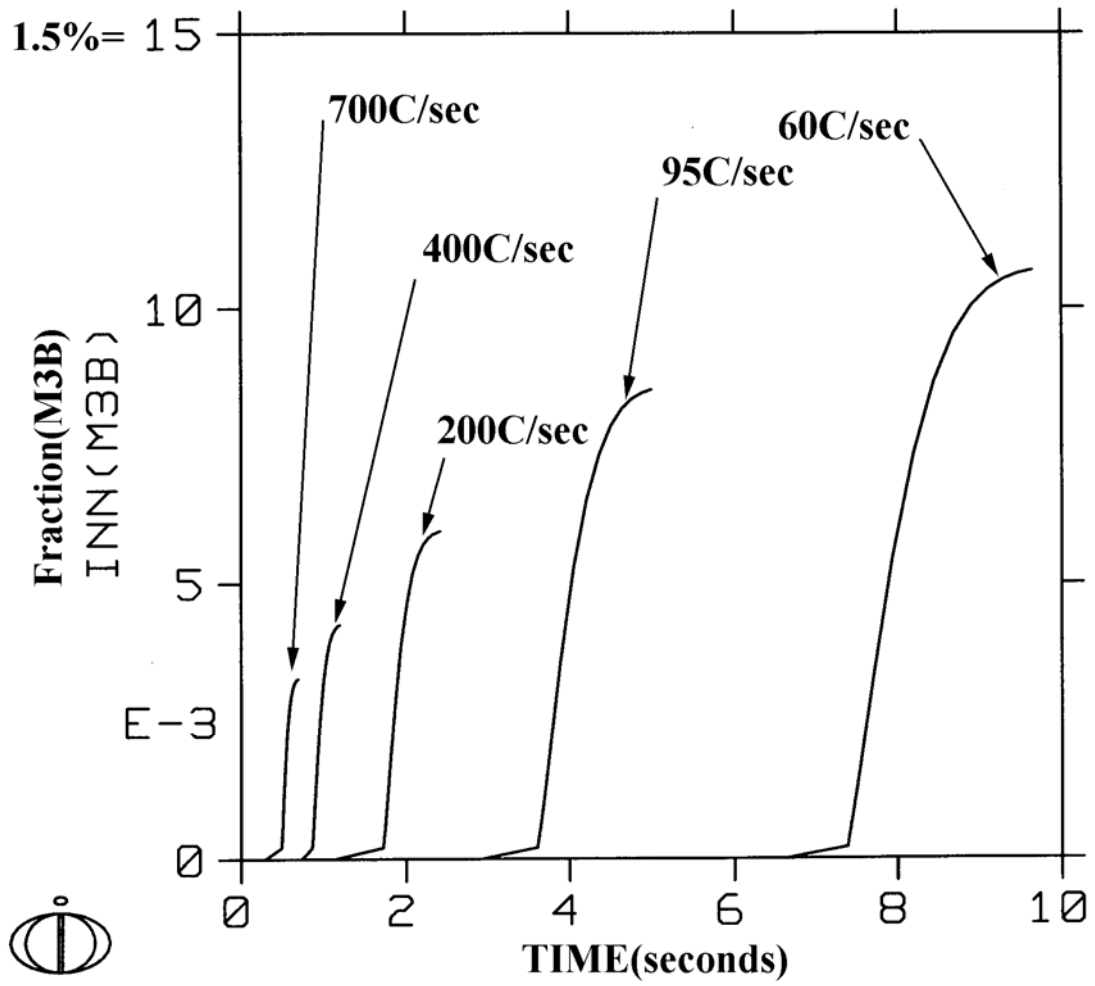
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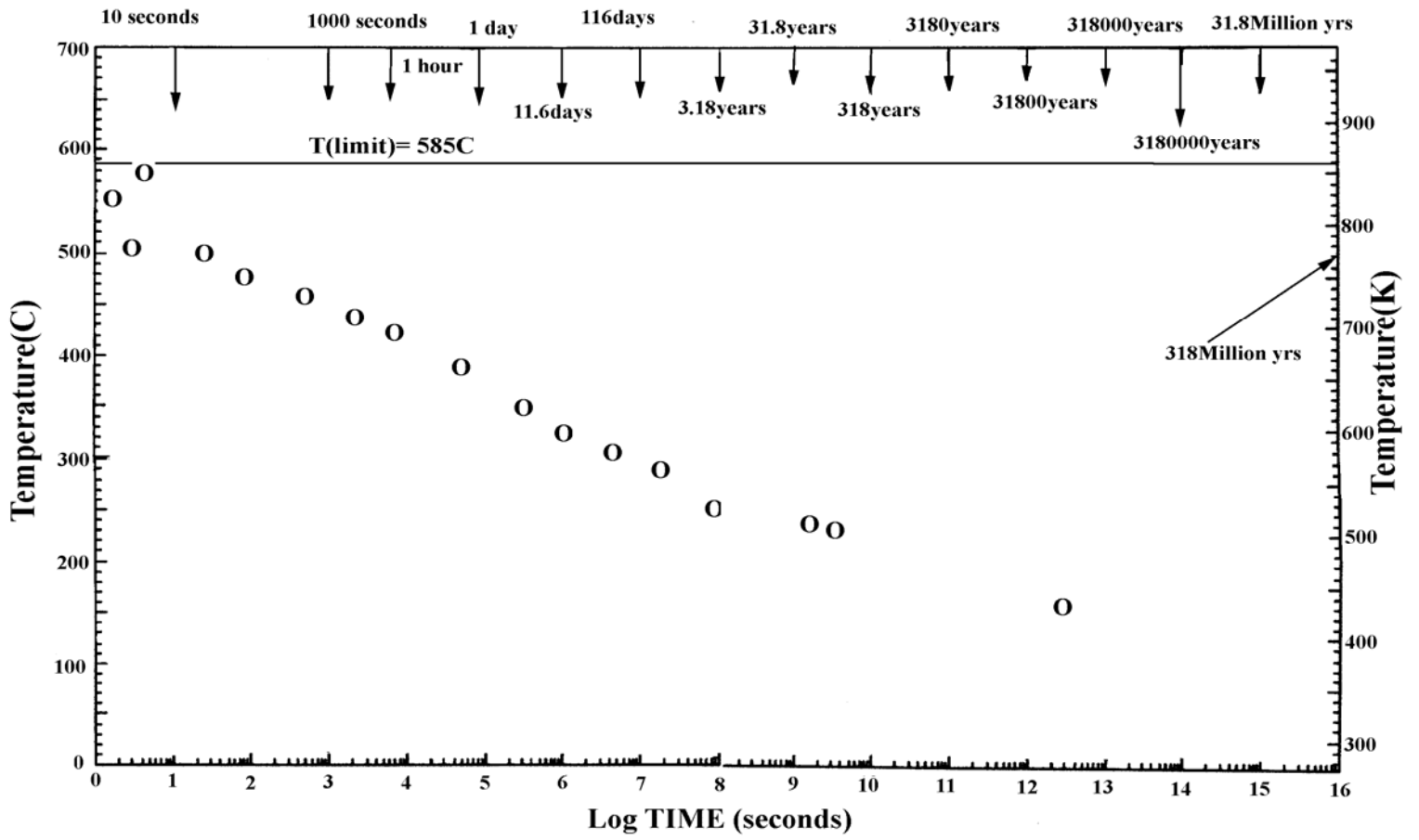
Equilibrium Calculation for SAM2X5





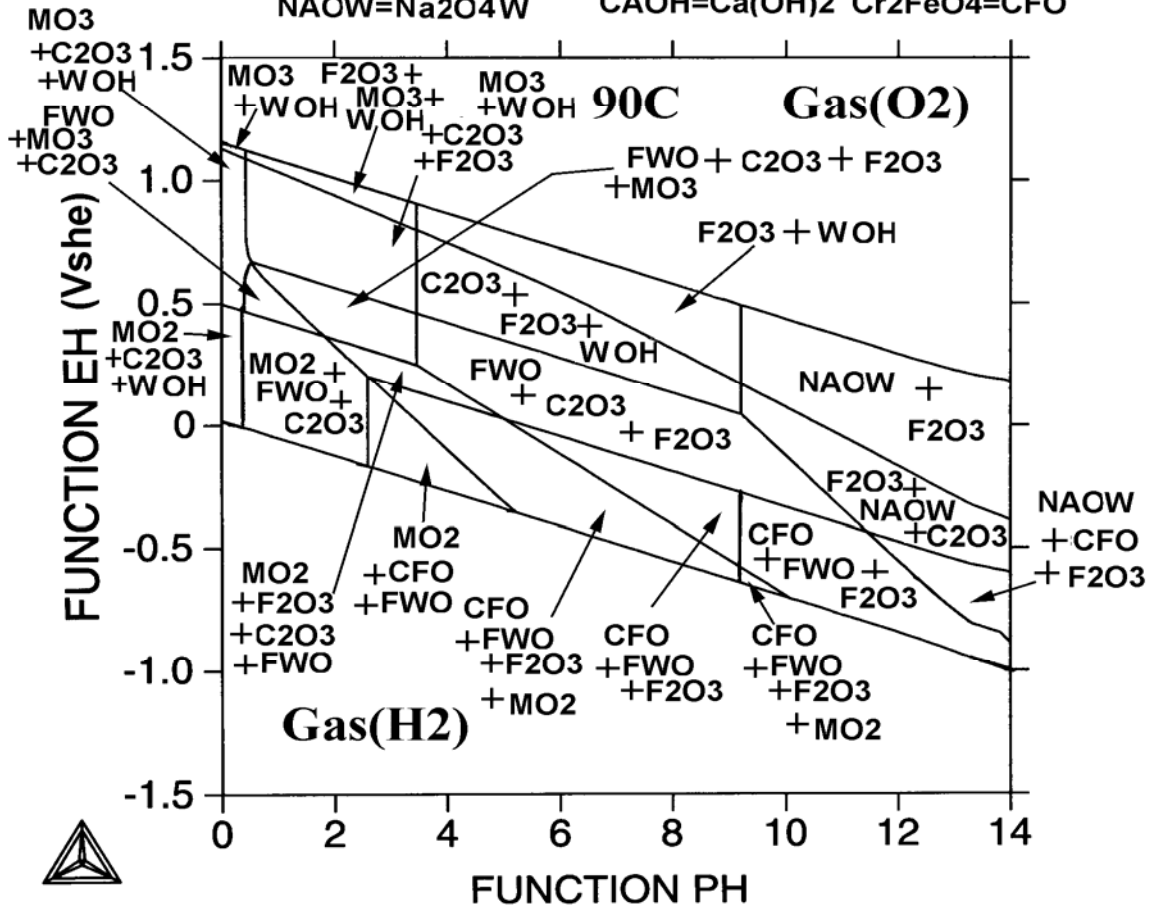


Calculated Continuous Cooling Curves for SAM 7

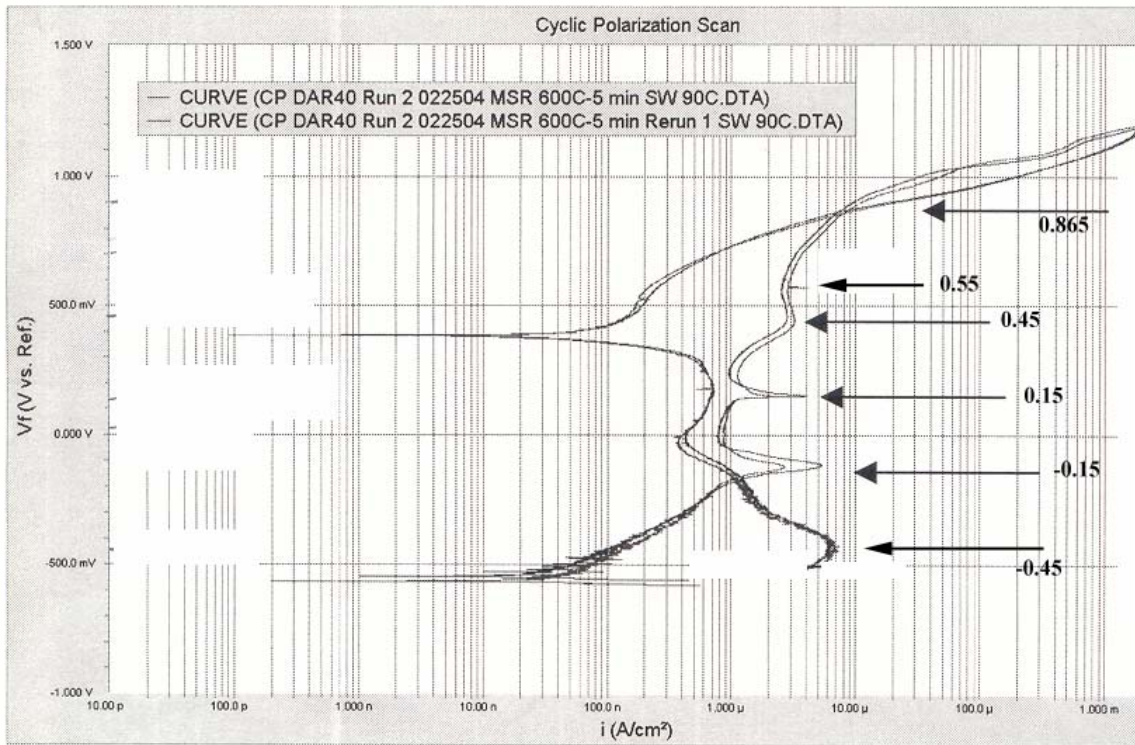


Calculated Transformation vs. Time Curve for Amorphous SAM 7 to 1% M₃B

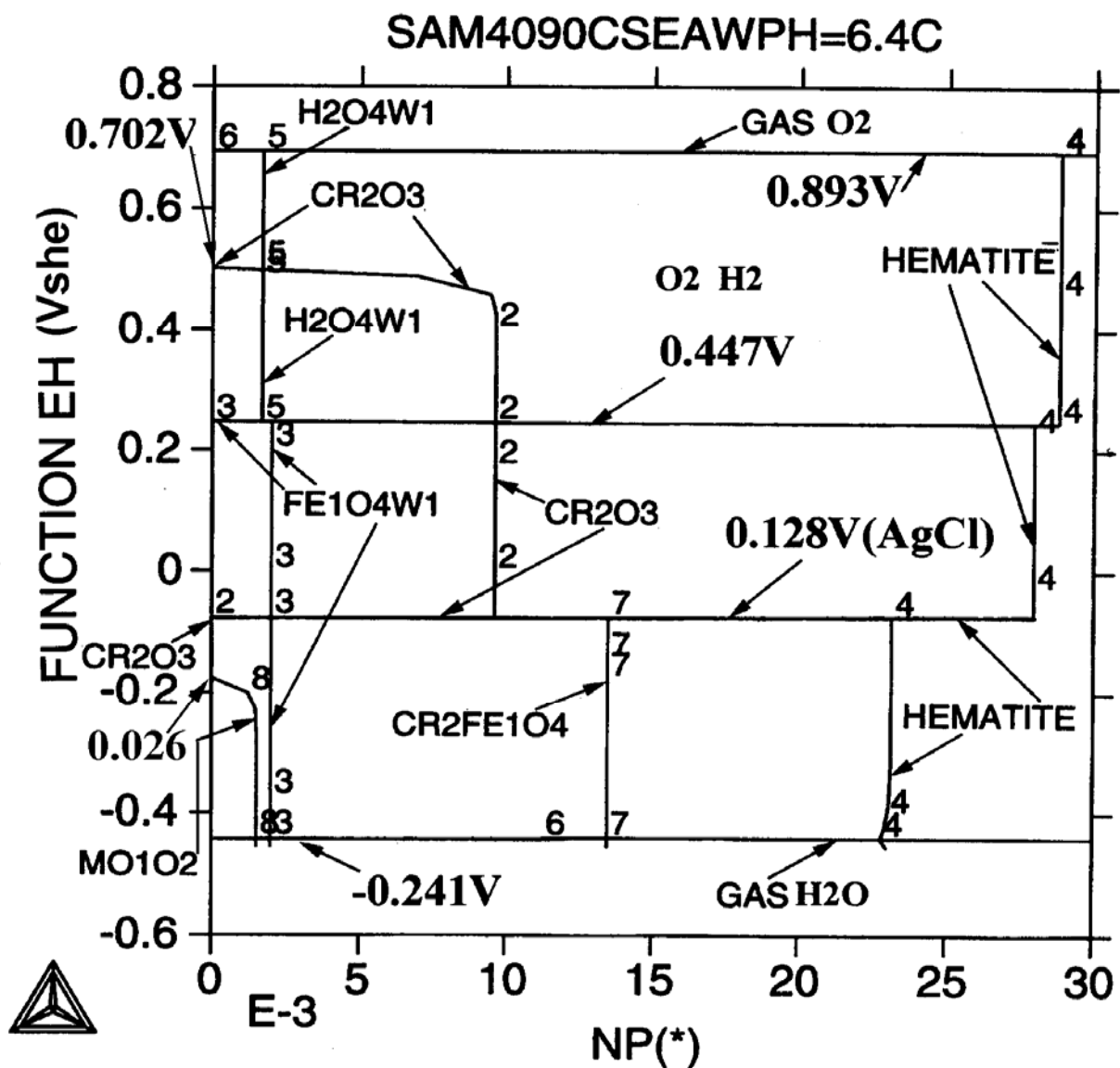
$\text{CaCO}_3 = \text{CACO}$ $\text{CWO} = \text{CaO} \cdot \text{WO}_3$ $\text{CaO(OH)} = \text{COH}$ $\text{CaO} \cdot \text{MO}_3 = \text{CMO}$
 $\text{MO}_3 = \text{MoO}_3$ $\text{Fe}_3\text{O}_4 = \text{F}_3\text{O}_4$ $\text{FWO} = \text{FeWO}_4$
 $\text{MO}_2 = \text{MoO}_2$ $\text{WOH} = \text{WO}_2(\text{OH})_2$ $\text{Cr}_2\text{O}_3 = \text{C}_2\text{O}_3$ $\text{Fe}_2\text{O}_3 = \text{F}_2\text{O}_3$
 $\text{NAOW} = \text{Na}_2\text{O}_4\text{W}$ $\text{CAOH} = \text{Ca(OH)}_2$ $\text{Cr}_2\text{FeO}_4 = \text{CFO}$



Calculated Pourbaix Diagram at 90C in SeaWater for SAM 40 Fe-2.5 at%Mo-19a%Cr-4a%C-16 -a%B and 1.7a% W. The Si and Mn are omitted. The calculations describe a solution containing 1000 grams of H₂O , 0.68 moles of NaCl(4 wt%) and one gram of alloy. Hematite is Fe₂O₃.



Cyclic Polarization measurements for a melt spun ribbon (MSR) sample of Amorphous SAM 40[1-7] Figures 1 and 3 display the Pourbaix Diagram and EH vs $Np(*)$ calculation performed for comparison with Figure 2. As indicated above the pretest measured pH was 7.4 while the post test value was 6.4. The specific features of the measured voltages are to be compared with the calculated values shown in Figure 3. This sample was annealed at 600C for 5 minutes. This comparison yields the following: 0.865 Volts compares with the calculated formation of O_2 gas as the voltage is increased above 0.893 Volts, 0.55 Volts compares with the calculated dissolution of Cr_2O_3 as the voltage increases above 0.702 Volts. The observed anodic peak at 0.45 Volts compares with the calculated transformation at 0.447 Volts of $FeO.WO_3$ to $WO_2.(OH)_2$ and Fe_2O_3 as voltage is increased. Similarly the anodic peak at 0.15 Volts compares well with the calculated transformation of Cr_2O_3 plus Fe_2O_3 to Cr_2FeO_4 at 0.128 Volts as the voltage decreases. The next prominent peak appears at -0.15 Volts which compares with the calculated dissolution of MoO_2 at 0.026 Volts as the voltage increases. Finally the anodic peak -0.45 Volts compares with the calculated formation of H_2O gas at -0.241 Volts.



Calculated Voltage, EH vs Phase Fraction relations at 90C in SeaWater, at pH=6.4 for SAM 40, Fe-2.5at%Mo-19a%Cr-4a%C-16 -a%B and 1.7a% W. The Si and Mn are omitted. The calculated Voltage vs. Phase Fraction (NP(*) in 0.001 moles) displayed in Figure 3 provides the voltage relative to the Standard Hydrogen Electrode. At 25C the voltage measured relative to the Ag/AgCl in a saturated KCl solution would be 0.197 volts higher according to D.J.G Ives and G.J.Janz. "Reference Electrodes", Academic Press, New York, 1961. The calculations are carried out for a solution containing 1000 grams of H₂O and 0.68 moles of NaCl and one gram of alloy. Figure 3 calculates that there are just below 0.029 moles of Fe₂O₃ (HEMATITE) present under the voltage conditions shown at equilibrium.

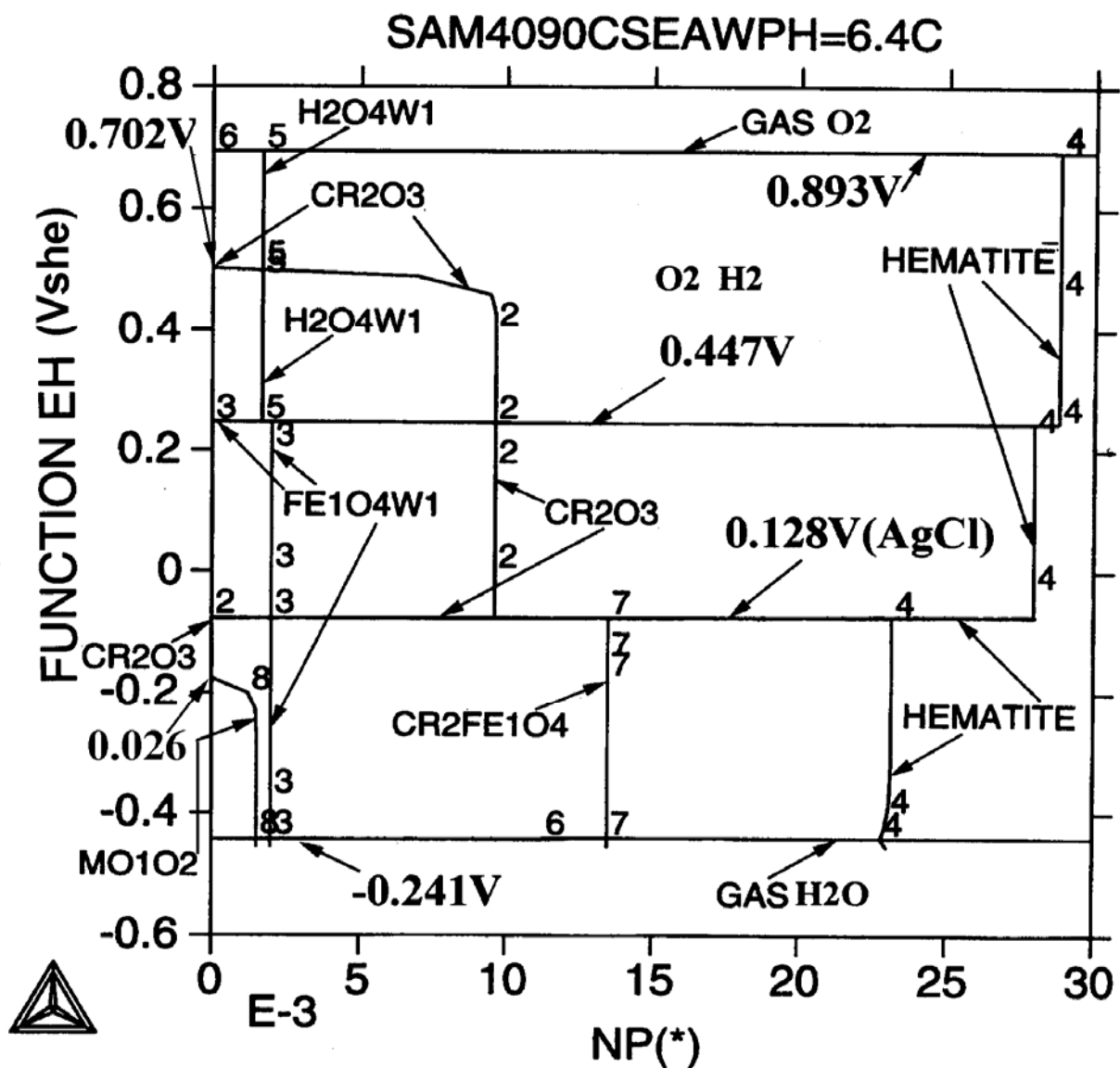


Fig 3. Calculated Voltage ,EH vs Phase Fraction relations at 90C in SeaWater, at pH=6.4 for SAM 40, Fe-2.5at%Mo-19a%Cr-4a%C-16 -a%B and 1.7a% W. The Si and Mn are omitted. The calculated Voltage vs. Phase Fraction (NP(*) in 0.001 moles) displayed in Figure 3 provides the voltage relative to the Standard Hydrogen Electrode. At 25C the voltage measured relative to the Ag/AgCl in a saturated KCl solution would be 0.197 volts higher according to D.J.G Ives and G.J.Janz. "Reference Electrodes", Academic Press ,New York ,1961 The calculations are carried out for a solution containing 1000 grams of H₂O and 0.68 moles of NaCl and one gram of alloy. Figure 3 calculates that there are just below 0.029 moles of Fe₂O₃ (HEMATITE) present under the voltage conditions shown at equilibrium.

